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Effectiveness of activated carbon disk for the analysis of iodine in water samples using wavelength dispersive X-ray fluorescence spectrometry

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HIGHLIGHTS

- A novel approach for the analysis of iodine in water samples was developed.
- Iodine preconcentrated on the AC disk was directly analyzed using WDXRF spectrometry.
- The AC disks were sufficiently durable for repeatable measurements until 8 days.
- The accuracy of the proposed AC-WDXRF method was confirmed by spike tests.

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ABSTRACT

A novel approach using wavelength dispersive X-ray fluorescence (WDXRF) spectrometry combined with an activated carbon (AC) disk was developed for the determination of total iodine concentrations in water samples. Dissolved iodine species (i.e., I^- and IO_3^-) in water samples were preconcentrated on the AC disk and directly analyzed by WDXRF spectrometry. The adsorption behavior of I^- and IO_3^- on the AC disk was assessed at varying pH levels (4, 6, and 8). The AC disks completely retained the I^- and IO_3^- for all the pH levels tested. The calibration curve obtained from the iodine concentrations (i.e., 0, 20, 200, and 400 μg) of AC disks and the measured X-ray intensity from the WDXRF analysis showed a good linearity ($R^2 = 0.9960$), with a relatively low limit of detection (0.575 μg). The durability of the AC disk for repeatable measurements was also assessed to validate the sustainability of the proposed method and consequently the measured X-ray intensity for the AC disks was constant until 8 d of analysis time. The accuracy of the proposed AC-WDXRF method was confirmed by measuring iodine concentration spiked in drinking water using inductively coupled plasma-mass spectrometry (ICP-MS). The proposed method is simple, rapid, efficient, and environmental friendly for iodine analysis in water samples. As a precursor of disinfection by products (DBPs), it is important to determine the total iodine concentrations in raw water.

1. Introduction

Although iodine is an essential micronutrient for all mammals, including human (Gilfedder et al., 2009), it has received considerable attention in the field of water/wastewater treatment. Iodine concentrations of 45–90, 2–20, and 0.5–20 μg L^{-1} in seawater, river water, and fresh water were commonly reported in the UK (Whitehead, 1979, 1984). During disinfection process in water treatment facilities, iodide (I^-) can be oxidized by the disinfectants (e.g., ozone (O_3), chlorine, and chloramine) to hypoiodous acid (HOI) and/or hypoiodite (OI^-), which can further react with natural organic matter (NOM) to form iodinated disinfection by products (I-DBPs) in source water with a high I^- concentration (Bichsel and von Gunten, 1999; Richardson et al., 2008). I-DBPs are currently regulated in the US owing to their higher toxicities than those of chlorinated and brominated DBPs (Plewa et al., 2004; Krasner et al., 2006). Therefore, determination of total iodine contents in source water is imperative in order to assess the iodine levels that can participate in the formation of I-DBPs.

Recently, X-ray fluorescence (XRF) analysis combined with a preconcentration method using solid phase extraction (SPE) disks has been widely applied to determine various elements in aqueous samples. Because XRF spectrometry is a suitable method for the direct analysis of elements in solid samples, preconcentration procedures with thin SPE disks may be ideal method to make sample

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specimen prior to XRF analysis (An et al., 2013, 2014; Margui et al., 2008, 2012). In previous studies (An et al., 2013, 2014), anion and cation exchange disks have been employed as solid sorbents to retain elements such as bromine and methylated arsenic (i.e., dimethylarsinic acid) in water samples, respectively. Furthermore, active thin layer and chelating disks have also been used to collect metal cations present in different aqueous matrices (Margui et al., 2008, 2012). With the use of these combined techniques, the direct quantitative determination of various elements retained in solid sorbents is possible, and therefore the elution step can be avoided.

In this study, we proposed a new method for rapid determination of total iodine contents in water samples by wavelength dispersive X-ray fluorescence (WDXRF) analysis after employing a preconcentration procedure using activated carbon (AC) disks as a follow-up and extension research of An et al. (2014). The retention behavior of I^- and iodate (IO_3^-), dominant species existing in natural waters, on AC disks was assessed at different pH levels to validate the suitability of the preconcentration method for iodine analysis. The calibration curve for different iodine concentrations retained on the AC disk was established, and the limit of detection (LOD) and method detection limit (MDL) were determined. The iodine concentrations spiked in drinking water samples were assessed to verify the accuracy of the proposed method. The AC-WDXRF method aims to decrease the analysis time and eliminate complicated pretreatment procedures for the rapid analysis of iodine in water samples. The effectiveness of this study is demonstrated by the fact that iodine, as a precursor of I-DBPs in raw water, can be rapidly determined using the proposed method. It enables us to establish an appropriate management plan.

2. Materials and methods

2.1. SPE disk

AC (model 2272) and anion exchange (AX, model 2252) disks obtained from 3M Empore (St. Paul, MN, USA), with a diameter of 47 mm and a thickness of 0.5 mm, were used to preconcentrate the I^- and IO_3^- in water samples. The properties of the AC disk were as follows: surface area >1100 $mm^2\,g^{-1}$, particle size 10 μm, and nominal carbon mass 50 mg. The AC surface is consists of a complex combination of positive and negative charges, providing adsorption and retention capacities of soluble and volatile analytes. The AX disk was based on polystyrene divinylbenzene with quaternary ammonium of functional groups. Both disks were conditioned prior to use in accordance with manufacturer's instructions. The AC disk was sequentially conditioned using 5 mL of methanol and deionized (DI) water. The AX disk was prepared with 10 mL of acetone, methanol, DI water, and 1 M sodium hydroxide. The extraction of I^- and IO_3^- in water samples using the AC and AX disks was performed by simple vacuum filtration.

2.2. Instruments

The concentration of iodine retained on AC disks was determined using WDXRF spectrometry (PW 2404, Phillips, Netherlands). The camber of X-ray pathway was set in a vacuum state to prevent signal loss due to air absorption. The inductively coupled plasma-mass spectrometry (ICP-MS) (Agilent 7700S, Agilent Technologies, Japan) was employed to confirm the iodine concentrations in water samples as reference values. A tuning solution was preliminarily used to optimize the analytical sensitivity prior to the analysis. Detailed instrumental conditions of WDXRF and ICP-MS systems used in this study are presented in Table 1.

Table 1
Instrumental conditions for the iodine analysis.

Parameter	Measurement condition
Wavelength dispersive X-ray fluorescence (WDXRF) spectrometry	
X-ray tube	Rhodium (Rh) target (30 kV, 100 mA)
Diffraction crystal	LiF 220 (thickness = 0.2848 nm)
Window	Be window
Collimator	300 μm
Detector	Flow type
Peak angle	102.85 (°2θ) for I-Lα line
Offset background	−1.8916 (°2θ)
Analysis time	100 s
Inductively coupled plasma-mass spectrometry (ICP-MS)	
RF power	1550 W
Plasma gas flow rate	Ar 1.1 L min^{-1}
Extract 1 and 2 lens voltage	−8.3 V for extract 1 and −195 V for extract 2
Omega lens voltage	11.9 V
Torch	Standard Quartz 2.5 mm
Nebulizer	Micromist
Sampling and skimmer cone	Nickel
Integration time	0.33 s
Monitored mass	167 m/z

2.3. Effect of pH on the retention behavior of I^- and IO_3^- on the AC disk

The retention behavior was evaluated at different pH levels in order to test the suitability of the AC disks for the preconcentration of I^- and IO_3^- in water samples. Ammonium iodide (NH_4I, Junsei, Japan) and potassium iodate (KIO_3) solution (Fluka, Switzerland) were used to prepare stock solutions by dilution with DI water. Solutions containing 1 mg L^{-1} of iodine with different pH levels (i.e. 4, 6, and 8) were prepared and 20 mL of each solution was passed through the AC disks. The pH was adjusted by adding appropriate amounts of 1 N NaOH and HNO_3. The total amount of iodine retained on the disk was calculated from the difference of the iodine concentrations between in the initial solution and effluent determined using ICP-MS analysis.

2.4. Calibration standards

The AC disks were prepared with different iodine concentrations (0, 20, 200, and 400 μg) by passing 20 mL of 0, 1, 10, and 20 mg L^{-1} iodine solutions to make the calibration standards. After drying at 60 °C for 5 min, the preconcentrated AC disks were directly analyzed using WDXRF spectrometry in order to establish the calibration curve. Before exposing to X-ray, the AC disks were coated with X-ray film (Chemplex®, SE Waaler St. Stuart, FL, USA) in order to prevent damage to the AC disk surface from the X-ray irradiation (Abe et al., 2006). It was confirmed that the intensity of the X-ray emitted from iodine is not absorbed by X-ray film because of its high energy. The LOD and MDL values were calculated and compared to those of other conventional methods to assess analytical sensitivity. The LOD and MDL values were defined as three times the standard deviation of blank measurements (σ_b) divided by the slope of the calibration line (p) and the standard deviation of seven replicates of sample measurements (σ_S) multiplied by Student's t-value at the 99% confidence level ($t = 3.143$ at 6 degrees of freedom), respectively (Zorn et al., 1999; ICH, 1999).

2.5. Application to drinking water sample

Drinking water samples were used for the spike tests in order to confirm the applicability of the proposed AC-WDXRF method. The water sample contained 144 μg L^{-1} of total organic carbon (TOC). The water samples were spiked with NH_4I stock solution to make 1 and 5 mg L^{-1} iodine concentrations. Afterwards, 20 mL of the spiked samples was filtered through the AC disk and total iodine